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<p>(21) International Application Number: PCT/EP95/01992</p> <p>(22) International Filing Date: 24 May 1995 (24.05.95)</p> <p>(30) Priority Data: P 44 18 728.9 28 May 1994 (28.05.94) DE 195 03 171.7 1 February 1995 (01.02.95) DE</p> <p>(71) Applicant (for all designated States except US): ISOVER SAINT-GOBAIN [FR/FR]; Les Miroirs, 18, avenue d'Alsace, F-92400 Courbevoie (FR).</p> <p>(72) Inventors; and (75) Inventors/Applicants (for US only): ROUYER, Elisabeth [FR/FR]; 32bis, rue de l'Alma, F-92600 Asnières (FR). DE MERINGO, Alain [FR/FR]; 294, rue Saint-Jacques, F-75005 Paris (FR). MAUGENDRE, Stéphane [FR/FR]; 21, rue Gaston Watteau, F-60460 Prény-sur-Oise (FR). SAINTE-FOI, Daniel [FR/FR]; 56, rue Marcel Duchemin, F-60600 Clermont (FR).</p> <p>(74) Agent: KADOR & PARTNER; Corneliusstrasse 15, D-80469 München (DE).</p>		<p>(81) Designated States: AU, BR, CA, CN, CZ, FI, HU, JP, KR, MX, NO, NZ, PL, SI, SK, US, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).</p> <p>Published With international search report.</p>
<p>(54) Title: GLASS-FIBER COMPOSITIONS</p>		
<p>(57) Abstract</p> <p>A biologically degradable mineral-fiber composition characterized by the following constituents in percent by weight: SiO₂ 45 to 60; Al₂O₃ less than 2; CaO + MgO 10 to 16; Na₂O + K₂O 14 to 20; B₂O₃ 7 to 18; P₂O₅ 0 to 4; BaO 1 to 5; Ti, Zr, Zn, Sr, Fe, Mn oxide 0 to 1.5; Diverse up to 0.5.</p>		

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Glass-fiber compositions

The present invention relates to a glass-fiber composition that is biologically degradable.

The prior art describes some glass-fiber compositions which are said to be biologically degradable.

The biological degradability of glass-fiber compositions is of great importance because various studies point out that some glass fibers with very small diameters in the range of less than 3 microns are suspected to be carcinogenic, while biologically degradable glass fibers of such dimensions show no carcinogenicity.

However not only the biological degradability is of crucial importance but also the mechanical and thermal properties of the glass fibers, or the products produced therefrom, the resistance of the glass fibers and the processibility of the glass-fiber composition. For example glass fibers are used to a great extent for insulation purposes. For these applications sufficient moisture-resistance is necessary.

Also, the glass-fiber composition must permit processibility by known methods for producing glass fibers with a small diameter, for example the centrifugal technique, in particular the inner centrifugal technique (this technique is described for example in US-PS 4 203 745).

The invention is based on the problem of providing a novel glass-fiber composition that is characterized by biological degradability, has good stability or resistance to moisture and is easy to process.

The invention is based on the finding that this problem can be solved by a glass-fiber composition that substantially has considerable amounts of alkaline-earth oxide, alkali oxide and boron oxide and also contains barium oxide.

It has turned out that such a glass-fiber composition fulfills the combination of the necessary properties, namely

biological degradability, resistance to moisture and good processibility.

The object of the invention is a glass-fiber composition that is biologically degradable, characterized by the following constituents in percent by weight:

SiO_2	45	to 60
Al_2O_3	less than 2	
$\text{CaO} + \text{MgO}$	10	to 16
$\text{Na}_2\text{O} + \text{K}_2\text{O}$	14	to 20
B_2O_3	7	to 18
P_2O_5	0	to 4
BaO	1	to 5
Ti, Zr, Zn, Sr, Fe, Mn oxide	0	to 1.5
Diverse		up to 0.5.

The inventive glass-fiber compositions are processible by the centrifugal technique. The obtained fibers have good resistance to moisture. Surprisingly enough, the glass-fiber compositions show biological degradability. The mean fiber diameter is preferably less than 10 microns and is in particular between 2.5 and 5 microns.

The inventive glass-fiber compositions preferably have the following constituents in percent by weight:

SiO_2	53	to 60
Al_2O_3	0	to 1.5
$\text{CaO} + \text{MgO}$	10	to 13
$\text{Na}_2\text{O} + \text{K}_2\text{O}$	14	to 18
B_2O_3	8	to 14
P_2O_5	0	to 2.0
BaO	1.5	to 3
Ti, Zr, Zn, Sr, Fe, Mn oxide	0	to 1.5
Diverse		up to 0.5.

According to a further preferred embodiment the inventive glass-fiber compositions have the following constituents in percent by weight:

SiO_2	46 to 55
Al_2O_3	less than 2
$\text{CaO} + \text{MgO}$	10 to 14
$\text{Na}_2\text{O} + \text{K}_2\text{O}$	14 to 17
B_2O_3	10 to 17
P_2O_5	0 to 2.0
BaO	3 to 5
Ti, Zr, Zn, Sr, Fe, Mn oxide	0 to 1.5
Diverse	up to 0.5.

Barium oxide has a positive influence on moisture-resistance and presumably also on biological degradability.

The inventive compositions can contain up to 1.5 percent by weight titanium oxide, zirconium oxide, zinc oxide, strontium oxide, lithium oxide, iron oxide and/or manganese oxide. Mixtures of 2 or 3 of these oxides are particularly preferred.

Phosphorus oxide is preferably present in an amount of 0.1 to 2 percent by weight, in particular 0.3 to 1.5 percent by weight. Phosphorus oxide has a positive influence on biological degradability.

According to a preferred embodiment the composition contains less than 2 percent by weight magnesium oxide.

The moisture-resistance of the inventive glass-fiber compositions was determined by a standard method known as the DGG method. In the DGG method 10 g finely ground glass with a grain size between about 360 and 400 microns is held at the boiling point for five hours in 100 ml water. After quick cooling of the material the solution is filtered and a certain volume of the filtrate evaporated to dryness. The weight of the thus obtained dry material permits the amount

of glass dissolved in the water to be calculated. The amount is stated in milligrams per gram of tested glass.

The biological degradability of the inventive glass compositions was tested by introducing 1 g of the glass powder, as described for the DGG method, into a physiological solution with the composition stated below and a pH value of 7.4:

NaCl	6.78
NH ₄ Cl	0.535
NaHCO ₃	2.268
NaH ₂ PO ₄ · H ₂ O	0.166
(Na ₃ citrate) 2H ₂ O	0.059
Glycine	0.450
H ₂ SO ₄	0.049
CaCl ₂	0.022

Dynamic test conditions were selected as are described in Scholze and Conradt. The flow rate was 300 ml/day. The duration of the test was 14 days. The results are stated as percent of SiO₂ in the solution x 100 after 14 days.

The invention shall be described in more detail in the following with reference to examples.

Example 1

A glass of the following composition in percent by weight was melted:

SiO ₂	57.5
Al ₂ O ₃	0.5
CaO	8.0
MgO	3.5
Na ₂ O	15.8
K ₂ O	0.2

B ₂ O ₃	12.0
BaO	2.0
Diverse	0.5.

These glass compositions could be processed by the centrifugal technique.

Using the above-described DGG method a value of 40 was determined.

The above-described test for biological degradability yielded a value of 500.

Example 2

A glass with the following composition in percent by weight was melted:

SiO ₂	56.5
Al ₂ O ₃	0.5
CaO	8.0
MgO	3.5
Na ₂ O	15.8
K ₂ O	0.2
B ₂ O ₃	12.0
BaO	2.0
P ₂ O ₅	1.0
Diverse	0.5.

These glass compositions could be processed by the centrifugal technique.

Using the above-described DGG method a value of 40 was determined.

The above-described test for biological degradability yielded a value of 600.

Example 3

A glass with the following composition in percent by weight was melted:

SiO ₂	57.2
Al ₂ O ₃	0.8
CaO	7.0
MgO	2.0
Na ₂ O	18.0
K ₂ O	0.5
B ₂ O ₃	12.5
BaO	2.0.

These glass compositions could be processed by the centrifugal technique.

Using the above-described DGG method a value of 20 was determined.

The above-described test for biological degradability yielded a value of 500.

Example 4

A glass with the following composition in percent by weight was melted:

SiO ₂	57.2
Al ₂ O ₃	0.8
CaO	8.0
MgO	1.5
Na ₂ O	17.5
K ₂ O	0.5
B ₂ O ₃	13.0
BaO	1.5.

These glass compositions could be processed by the centrifugal technique.

Using the above-described DGG method a value of 20 was determined.

The above-described test for biological degradability yielded a value of 600.

Claims

1. A glass-fiber composition that is biologically degradable, characterized by the following constituents in percent by weight:

SiO_2	45	to 60
Al_2O_3	less than 2	
$\text{CaO} + \text{MgO}$	10	to 16
$\text{Na}_2\text{O} + \text{K}_2\text{O}$	14	to 20
B_2O_3	7	to 18
P_2O_5	0	to 4
BaO	1	to 5
Ti, Zr, Zn, Sr, Fe, Mn oxide	0	to 1.5
Diverse		up to 0.5.

2. The glass-fiber composition of claim 1, characterized by the following constituents in percent by weight:

SiO_2	53	to 60
Al_2O_3	0	to 1.5
$\text{CaO} + \text{MgO}$	10	to 13
$\text{Na}_2\text{O} + \text{K}_2\text{O}$	14	to 18
B_2O_3	8	to 14
P_2O_5	0	to 2.0
BaO	1.5	to 3
Ti, Zr, Zn, Sr, Fe, Mn oxide	0	to 1.5
Diverse		up to 0.5.

3. The glass-fiber composition of claim 1, characterized by the following constituents in percent by weight:

SiO_2	46	to 55
Al_2O_3	1.5	to 4
$\text{CaO} + \text{MgO}$	10	to 14
$\text{Na}_2\text{O} + \text{K}_2\text{O}$	14	to 17

B_2O_3	10	to 17
P_2O_5	0	to 2.0
BaO	3	to 5
Ti, Zr, Zn, Sr, Fe, Mn oxide	0	to 1.5
Diverse		up to 0.5.

4. The glass-fiber composition of any of claims 1 to 3, characterized in that the composition contains up to 1.5 percent by weight titanium oxide, zirconium oxide, zinc oxide, strontium oxide, lithium oxide, iron oxide, manganese oxide and mixtures thereof.

5. The glass-fiber composition of any of claims 1 to 4, characterized in that the composition contains 0.1 to 2 percent by weight, in particular 0.3 to 1.5 percent by weight, phosphorus oxide.

6. The glass-fiber composition of any of claims 1 to 5, characterized in that the composition contains less than 2 percent by weight magnesium oxide.

INTERNATIONAL SEARCH REPORT

Internat Application No
PCT/EP 95/01992

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C03C13/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C03C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP,A,0 588 251 (SCHULLER INTERNATIONAL, INC.) 23 March 1994 see claims 1-3; tables 1,2 ---	1-6
A	EP,A,0 019 600 (OY PARTEK AB) 26 November 1980 see claim 1 ---	1-6
A	EP,A,0 412 878 (ISOVER SAINT-GOBAIN) 13 February 1991 see claims --- -/-	1

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	<p>GLASTECHNISCHE BERICHTE, vol. 64, no. 1, January 1991 FRANKFURT DE, pages 16-28, XP 000178832 R. M. POTTER ET AL. 'Glass Fiber Dissolution in a Physiological Saline Solution' see page 26 - page 27; table 2 -----</p>	1

INTERNATIONAL SEARCH REPORT

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PCT/EP 95/01992

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP-A-588251	23-03-94	US-A- 5401693 CA-A- 2106412 JP-A- 6321578	28-03-95 19-03-94 22-11-94
EP-A-19600	26-11-80	SE-B- 418961 JP-C- 1195154 JP-A- 56014450 JP-B- 58024385 SE-A- 7904044 US-A- 4312952 US-A- 4381347	06-06-81 12-03-84 12-02-81 20-05-83 10-11-80 26-01-82 26-04-83
EP-A-412878	13-02-91	FR-A- 2650821 FR-A- 2658182 AU-B- 630484 AU-A- 6002590 CA-A- 2022446 CN-A, B 1049834 CN-A- 1093066 DE-D- 69007369 DE-T- 69007369 ES-T- 2053139 HU-B- 210633 JP-A- 3093650 PL-B- 165859 SI-A- 9011548 US-A- 5108957 US-A- 5250488	15-02-91 16-08-91 29-10-92 14-02-91 12-02-91 13-03-91 05-10-94 21-04-94 13-10-94 16-07-94 28-06-95 18-04-91 28-02-95 31-12-94 28-04-92 05-10-93